(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 375 695 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
02.01.2004 Bulletin 2004/01

(21) Application number: **02703886.8**

(22) Date of filing: **22.02.2002**

(51) Int Cl.[7]: **C23C 4/04**

(86) International application number:
PCT/JP2002/001600

(87) International publication number:
WO 2002/068706 (06.09.2002 Gazette 2002/36)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **28.02.2001 JP 2001055162**

(71) Applicants:
- **Nippon Piston Ring Co., Ltd.**
  Yono-City, Saitama 338-8503 (JP)
- **MAN B & W Diesel A/S**
  2450 Copenhagen SV (DK)

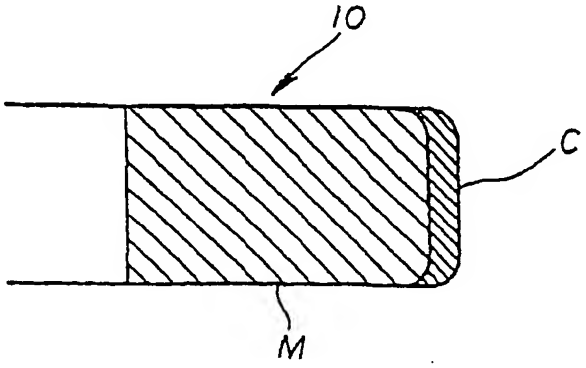
(72) Inventor: **TAKAMURA, Hiroyuki,**
Nippon Piston Ring Co., Ltd
Shimotsuga-gun, Tochigi 329-0114 (JP)

(74) Representative: **Munk, Ludwig, Dipl.-Ing.**
Patentanwalt
Prinzregentenstrasse 1
86150 Augsburg (DE)

(54) WEAR-RESISTANT SLIDING MEMBER

(57) A wear-resistant sliding member (10) which comprises a base metal (M) and a sprayed coating (C) formed by thermally spraying a mixed powder comprising, by mass, 30 to 70% of a molybdenum powder, 10 to 40% of a nickel-chrome alloy powder, 5 to 40% of a ceramics powder, and 2 to 15% of a solid lubricant onto a sliding surface of the base metal. The wear-resistant sliding member is excellent in wear-resistance and resistance to scuffing, and thus can be utilized in a large-sized marine diesel engine, which is used under severe conditions.

FIG.1



EP 1 375 695 A1

Description

Field of the Invention

[0001] The present invention relates to a wear-resistant sliding member, such as a piston ring and a cylinder liner for use in internal combustion engines.

Background of the Invention

[0002] Recently, internal combustion engines are strongly demanded to have higher power and performance. Sliding members, such as piston rings and cylinder liners employed in the internal combustion engines are burdened with ever increasing severe conditions, whereby every sliding member is required to have higher abrasion resistance and scuffing resistance.

[0003] Conventionally, chrome-plating treatment is applied to enhance the abrasion resistance of the sliding member. However, the chrome-plating treatment is insufficient to improve the scuffing resistance of the sliding member, so that it tends to be replaced by spraying treatments. For instance, a technique is proposed by JP 6-221438 A that forms a sprayed coating on the external circumferential sliding surface of a piston ring by means of plasma-spraying, where the sprayed coating comprises molybdenum, nickel-chrome alloy and fine powders of chrome carbide.

[0004] The piston ring as proposed above has a sliding resistance increased due to the ceramics powders contained in the sprayed coating. Furthermore, a problem exists that it would wear a cylinder liner, because the ceramics powders attack the counterpart material.

Summary of the Invention

[0005] The present invention is directed to solve the problems described above and provide an abrasion resistant sliding member formed with a sprayed coating that is prevented from increasing the sliding resistance and attacking the counterpart.

[0006] Thus, according to the present invention, a sliding member has a base metal and a sprayed coating formed on an external sliding surface of the base metal. The coating is made by spraying of a mixture containing, by mass, 30 to 70% of molybdenum powders, 10 to 40% of nickel-chrome alloy powders, 5 to 40% of ceramics powders, and 2 to 15% of solid lubricant powders.

[0007] The reason for a content range of 30 to 70% by mass of molybdenum powders is that, when the content of molybdenum powders below 30%, the coating deteriorates the scuffing resistance. When the content of molybdenum powders exceeds 70%, the coating is difficult to have a sufficient hardness.

[0008] The reason for a content range of 10 to 40% by mass of nickel-chrome alloy powders is that, when the content of nickel-chrome alloy powders below 10%, the coating is difficult to have a sufficient tenacity. When the content of nickel-chrome alloy powders exceeds 40%, the coating deteriorates the scuffing resistance.

[0009] The reason for a content range of 3 to 40% by mass of ceramics powders is that, when the content of ceramics powders below 3%, the coating is difficult to have a sufficient hardness. When the content of ceramics powders exceeds 40%, the coating becomes so hard to attack the counterpart.

[0010] The reason for a content range of 2 to 15% by mass of solid lubricant powders is that, when the content of ceramics powders below 2%, the lubrication effect is too insufficient to prevent the coating from increasing the sliding resistance and attacking the counterpart material. When the content of solid lubricant powders exceeds 15%, the coating becomes brittle.

[0011] The wear-resistant sliding member of the present invention is formed on the sliding surface thereof with the sprayed coating made by spraying of a mixture of molybdenum powders, nickel-chrome alloy powders, ceramics powders and solid lubricant powders, resulting in that it is superior both in abrasion resistance and in scuffing resistance and that it is less attackable to the counterpart material due to the solid lubricant powders contained in the coating than the sprayed sliding member as known by the aforementioned reference. Accordingly, it is advantageously employable as a piston ring or the like in high-performance, large-sized marine diesel engine. A special advantage is that it enables to lengthen life of engine.

Brief Description of the Drawings

[0012]

Fig. 1 is a partial, cross-sectional view of a piston ring according to the present invention.
Fig. 2 is a schematic drawing of a rotary-type plane sliding friction tester for performing various tests;

Fig. 3 is a graph showing a result of scuffing resistance tests; and
Fig. 4 is a graph showing abrasion amounts measured in the abrasion resistance tests.

Description of an Embodiment of the Invention

[0013] Referring to Fig. 1 showing a partial, cross-sectional view of a piston ring 10, according to an embodiment of the present invention, a sprayed coating C is formed on the external circumferential surface of the base metal M of the piston ring 10. The sprayed coating C is made by spraying a mixture containing, by mass, 30 to 70% of molybdenum powders, 10 to 40% of nickel-chrome alloy powders, 5 to 40% of ceramics powders, and 2 to 15% of solid lubricant powders.

[0014] The sprayed coating C is superior both in abrasion resistance and scuffing resistance while it is prevented from increasing the sliding resistance and attacking the counterpart material because of containing solid lubricant powders.

Examples

[0015] Now, embodiments of the sliding member, according to the present invention, are further described referring to various tests conducted in comparison with other sliding members.

[0016] Fourteen types of test samples were prepared by forming fourteen types of coating of 300 μm thickness on pieces of the same cast iron for piston rings, as a base material, of which the two samples Nos. 1 and 2 are comparative or corresponding to the other sliding members as known by the aforementioned reference. The twelve samples Nos. 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 are inventive or corresponding to the embodiments. The coatings were made by plasma-spraying of the respective powdery mixtures, of which the composition is shown in Table 1.

Table 1

Sample	Remarks	Composition of Powdery Mixture (mass %)			
		Mo	Ni-Cr alloy	Ceramics	Solid Lubricant
No.1	Comparative	45	20	35 (CrC)	
No.2	Comparative	65	30	5 (CrC)	
No.3	Inventive	40	15	30 (CrC)	15(CaF_2)
No.4	Inventive	60	30	5 (CrC)	5(CaF_2)
No.5	Inventive	40	15	30(Cr_2O_3)	15(CaF_2)
No.6	Inventive	60	30	5 (Cr_2O_3)	5 (CaF_2)
No.7	Inventive	40	15	30 (CrC)	15 (MnS)
No.8	Inventive	60	30	5 (CrC)	5 (MnS)
No.9	Inventive	40	15	30 (Cr_2O_3)	15 (MnS)
No.10	Inventive	60	30	5 (Cr_2O_3)	5 (MnS)
No.11	Inventive	40	15	30 (CrC)	15 (MoS_2)
No.12	Inventive	60	30	5 (CrC)	5 (MoS_2)
No.13	Inventive	40	15	30 (Cr_2O_3)	15 (MoS_2)
No. 14	Inventive	60	30	5 (Cr_2O_3)	5 (MoS_2)

[0017] Plasma-spraying conditions are as follows:
Gun: Sulzer Metco 7MB plasma spraying gun (product name)
Electric Voltage: 60 ~ 70V
Electric Current: 500A

[0018] Scuffing resistance and abrasion resistance tests were conducted for each specimens, as follows:

Scuffing resistance tests

[0019] Scuffing resistance for each sample was measured using a rotary-type plane sliding friction tester, as schematically shown in Fig. 2. The friction tester has a mechanism where a sample 11 is brought in contact with, and held pressed against, a rotary plane surface or counterpart material 12 rotating at a constant speed with a specified face pressure P for a specified period of time, and a face pressure at which scuffing occurs is measured as a critical scuffing face pressure. Face pressure was applied in a manner that initial face pressure of 2.45MPa was kept for 30 minutes,

then, the face pressure was increased by 0.98MPa in each successive 5 minutes.

[0020] Measuring conditions were as follows:

Sliding speed: 5m/sec

Lubricating oil: SAE30 + white kerosene (1:1)

Oil amount: no oil applied, except initial application

Counterpart material: Tarkalloy (known as a product name owned by Nippon Piston Ring Co., Ltd. for a boron cast iron)

[0021] A result for the tests is shown in Fig. 3. As seen from Fig. 3, all the inventive samples Nos. 3 to 14 have their critical scuffing face pressures in a range of 7.8 to 8.8 MPa while the comparative samples Nos. 1 and 2 have the critical scuffing face pressures in a range of 6.9 to 7.8 MPa. Accordingly, the inventive sliding member is similar or superior to the comparative one.

Abrasion resistance tests

[0022] Abrasion amounts for each sample and its counterpart material were measured using the aforementioned rotary type plane sliding friction tester, as schematically shown in Fig. 2. The friction tester has a mechanism where a sample 11 is brought in contact with, and held pressed against, a rotary plane surface of counterpart material 12 rotating at a constant speed with a specified face pressure P for a specified test running time. Lubricating oil is applied to the counter material 12.

[0023] Measuring conditions were as follows:

Sliding speed: 6m/sec

Face pressure: 6MPa

Lubricating oil: Spinox S-2 (known as a product name owned by Nippon Oil Co., Ltd. for bearing oiD

Oil temperature: 60±10°C

Oil amount: $10^{-4}m^3$ /min

Test running time: 100hr

Counterpart material: Tarkalloy (known as a product name owned by Nippon Piston Ring Co., Ltd. for a boron cast iron)

[0024] A result for the abrasion test is shown in Fig. 4. As seen from Fig. 4, all the inventive samples Nos. 3 to 14 have their abrasion amounts in a range of 12.6 to 17.1 μm while the comparative samples Nos. 1 and 2 have their abrasion amounts in a range of 17.5 to 22.3 μm. Accordingly, the inventive sliding member is better in abrasion resistance than the comparative one. All the inventive samples Nos. 3 to 14 have their counterpart abrasion amounts in a range of 1.1 to 2.1 μm while the comparative samples Nos. 1 and 2 have their counterpart abrasion amounts in a range of 2.8 to 4.3 μm. Accordingly, the inventive sliding member is much better in counterpart attacking resistance than the comparative one.

Claims

1. A sliding member (10) having a base metal (M) and a sprayed coating (C) formed on an external sliding surface of said base metal, **characterized in**

   that said coating is made by spraying of a mixture containing, by mass, 30 to 70% of molybdenum powders, 10 to 40% of nickel-chrome alloy powders, 3 to 40% of ceramics powders, and 2 to 15% of solid lubricant powders.

2. The sliding member as claimed in claim 1, wherein said ceramics powders comprise chrome oxide or chrome carbide.

3. The sliding member as claimed in either of claims 1 and 2, wherein said solid lubricant powders comprises at least one selected from the group constituting of calcium fluoride, manganese sulfide and molybdenum disulfide.

FIG.1

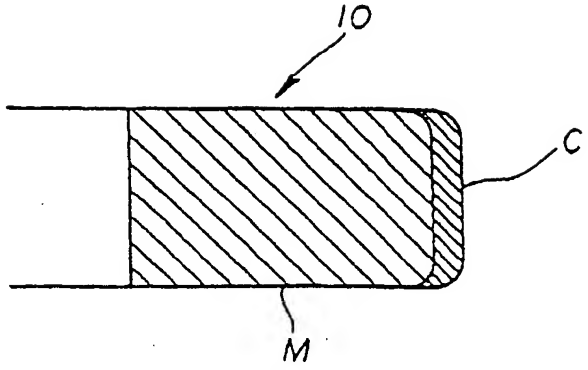


FIG.2

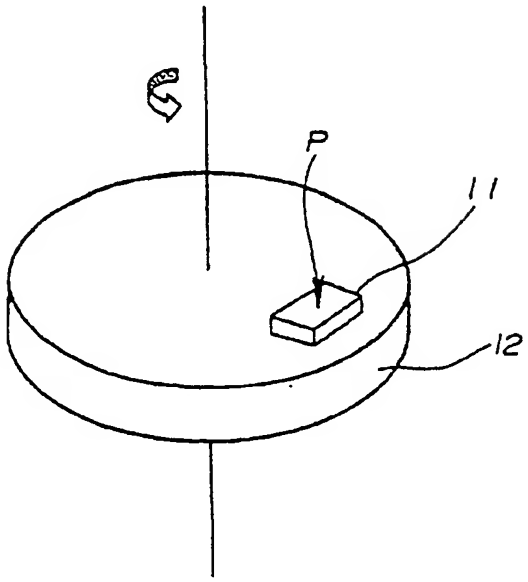


FIG.3

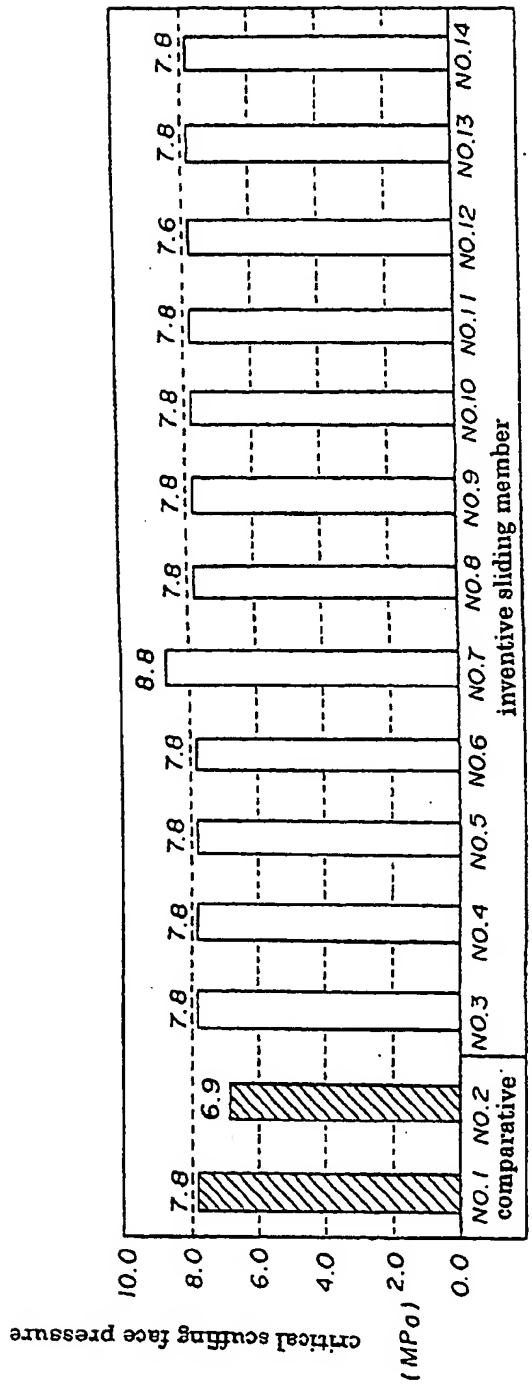
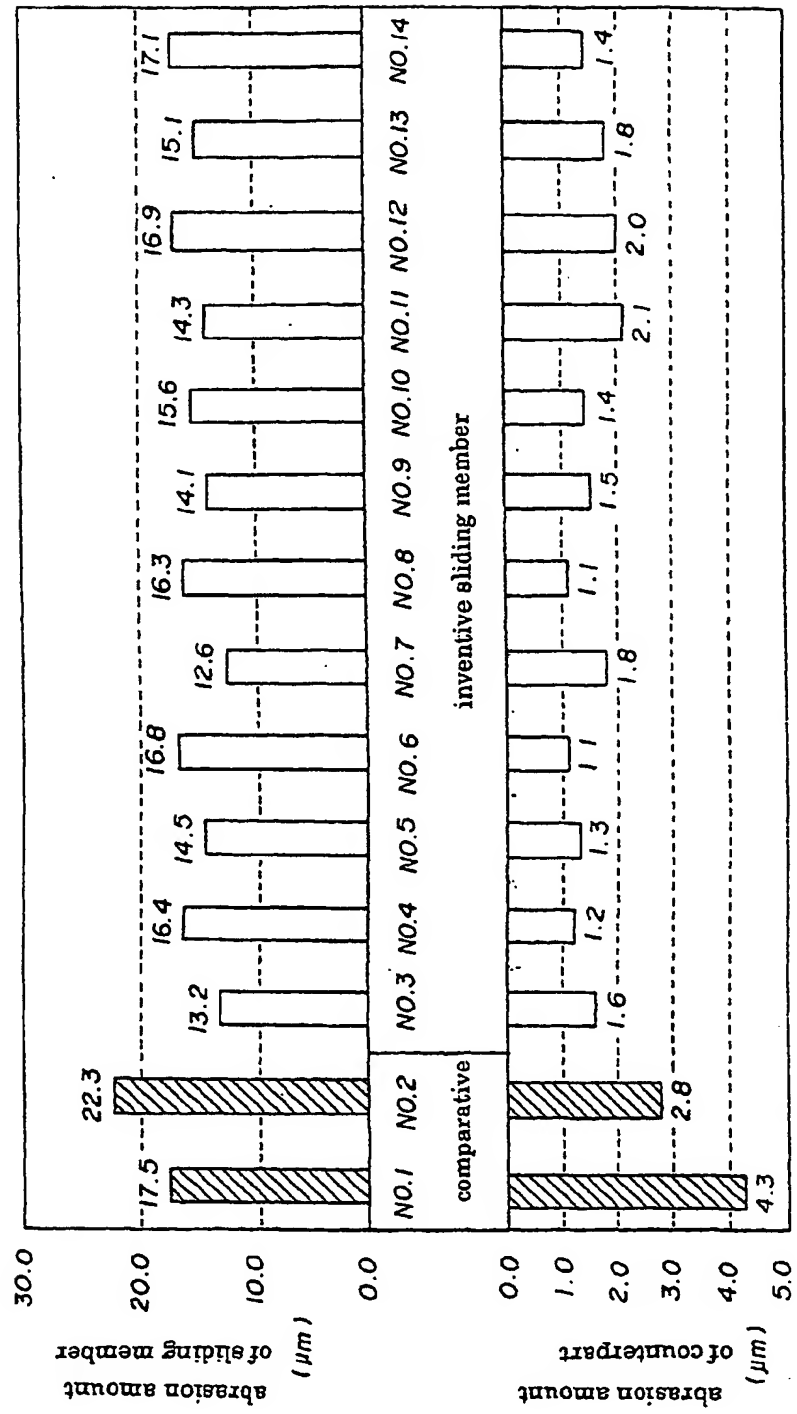

critical scuffing face pressure
(MPa)
10.0
8.0
6.0
4.0
2.0
0.0
7.8
6.9
7.8
7.8
7.8
7.8
8.8
7.8
7.8
7.8
7.8
7.6
7.8
7.8
NO.1
NO.2
NO.3
NO.4
NO.5
NO.6
NO.7
NO.8
NO.9
NO.10
NO.11
NO.12
NO.13
NO.14
comparative
inventive sliding member

FIG.4


abrasion amount of sliding member (μm)
30.0
20.0
10.0
0.0
abrasion amount of counterpart (μm)
0.0
1.0
2.0
3.0
4.0
5.0
NO.1
NO.2
NO.3
NO.4
NO.5
NO.6
NO.7
NO.8
NO.9
NO.10
NO.11
NO.12
NO.13
NO.14
comparative
inventive sliding member
17.5
22.3
13.2
16.4
14.5
16.8
12.6
16.3
14.1
15.6
14.3
16.9
15.1
17.1
4.3
2.8
1.6
1.2
1.3
1.1
1.8
1.1
1.5
1.4
2.1
2.0
1.8
1.4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/01600

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C23C4/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C23C4/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2002
Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9-202957 A (Nippon Piston Ring Co., Ltd.), 05 August, 1997 (05.08.97), (Family: none)	1-3
A	JP 57-76363 A (Mitsubishi Heavy Industries, Ltd.), 13 May, 1982 (13.05.82), (Family: none)	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 May, 2002 (13.05.02)	28 May, 2002 (28.05.02)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)